

PATENT SPECIFICATION

(11) 1264741

NO DRAWINGS

- (21) Application No. 15180/70 (22) Filed 31 March 1970
 (31) Convention Application No. 812375 (32) Filed 1 April 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 23 Feb. 1972
 (51) International Classification C 08 f 25/00
 (52) Index at acceptance
 C3P 12D1 12DX 12P1 12PX 12T
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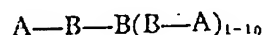


(54) NOVEL BLOCK COPOLYMERS HAVING TERMINAL RANDOM COPOLYMER BLOCKS OF STYRENE AND ALPHA-METHYL STYRENE

(71) We, SHELL INTERNATIONALE
 RESEARCH MAATSCHAPPIJ N.V., a company
 organised under the laws of The Netherlands,
 of 30 Carel van Bylandtlaan, The Hague,
 The Netherlands, do hereby declare the in-
 vention, for which we pray that a patent
 may be granted to us, and the method by
 which it is to be performed, to be particu-
 larly described in and by the following state-

The invention relates to a novel block co-
 polymer and a process for its preparation.

Block copolymers are copolymers with
 polymeric chains containing alternating blocks
 of homo- or copolymers, each block differing
 materially from the next adjacent block. They
 may be represented by the general formula



in which A and B represent polymer blocks.
 Adjacent blocks B are to be regarded as a
 single block. The simplest block copolymer
 has the structure A-B-A. In the general
 formula mentioned above A may be a poly-
 mer block of a monovinyl aromatic hydro-
 carbon and a polymer block of a conjugated
 diene.

Certain block copolymers, for example
 certain block copolymers of the structure poly-
 styrene - polyisoprene - polystyrene and poly-
 styrene - polybutadiene - polystyrene, show
 the unique feature that without being vul-
 canized they have at normal temperature
 elastomeric properties including strength pro-
 perties, comparable to those of conventional
 vulcanizates and are reversibly plastifiable.

The known block copolymers, however, are
 somewhat deficient in that they are sensitive
 to oxidation and also exhibit relatively poor
 high temperature performance.

Hydrogenation of the polymer blocks of
 the conjugated diene substantially improves
 the oxidation resistance but does little to im-
 prove the high temperature performance of
 the known block copolymers having terminal
 polystyrene blocks.

Block copolymers having terminal polymer
 blocks of alpha - methyl - styrene show im-
 proved high temperature performance in com-
 parison with those with terminal polymer
 blocks of styrene, but their processability is
 relatively poor compared with other elastom-
 ers. It is therefore necessary to raise the
 temperature at which such block copolymers
 are milled or otherwise processed. In such an
 event the rate of oxidation sharply increases
 and the block copolymers tend to degrade
 quite seriously. The hydrogenation of the
 diene blocks in such blocks copolymers re-
 duces this problem but a further problem still
 remains in the tendency of the alpha-methyl
 styrene polymer blocks to thermally depoly-
 merize.

It is an object of the present invention to
 provide block copolymers having alpha-methyl
 styrene units with improved thermal stabi-
 lity.

In accordance with the invention, a block
 copolymer is provided having the general con-
 figuration A-B-(B-A)₁₋₁₀, in which each
 A is a random copolymer block of styrene
 and alpha-methyl styrene having from 10
 to 40% of styrene units based on the total
 polymerized monomer units of the random co-
 polymer block, and each B is an elastomeric
 polymer block of a conjugated diene, a elas-
 tomeric polymer block of a hydrogenated
 conjugated diene or a polymer block of an
 alpha-mono-olefin.

The polymer block of the alpha mono-olefin
 may be elastomeric or resinous.

In the preferred types of block copolymers
 according to the invention, each A is a ran-
 dom copolymer block of styrene and alpha-
 methyl styrene having from 15 to 35 mol %
 of styrene units based on the total polymerized
 monomer units of the random copolymer
 block, the blocks A having an average mole-
 cular weight of between 2,000 and 50,000,
 and each B is a polymer block of an elastom-
 eric conjugated diene having an average

molecular weight of between 15,000 and 100,000.

Preferably the polymer blocks B are either elastomeric polymer blocks of an alpha-mono-olefin or elastomeric hydrogenated polymer blocks of a conjugated diene wherein at least 85% of the original unsaturation is reduced by hydrogenation. In the latter case the polymer blocks B are preferably elastomeric hydrogenated polyisoprene blocks but may also be elastomeric copolymer blocks of from 10 to 90 mol % of isoprene with from 90 to 10 mol % randomly disposed butadiene or homopoly-butadiene having from 35 to 55% 1,2 micro structure. Alternatively, the elastomeric diene polymer blocks may be copolymers of a diene with a minor proportion of randomly disposed styrene or alpha-methyl styrene units.

The block copolymers according to the invention may be linear or branched. They may be made by one of the following processes.

The block copolymers may be prepared by sequential formation of the polymer blocks. In this mode of preparation alpha-methyl styrene is polymerized together with styrene using a monofunctional catalyst, such as a lithium alkyl in a hydrocarbon medium modified with a polar activating compound such as an ether, mercaptan, or amine, typical of which are diethyl ether, tetrahydrofuran, secondary-butyl amine or methyl mercaptan. It is generally preferred to use relatively low polymerization temperatures in the order of -10°C to -100°C . It is preferred to start with all of the alpha-methyl styrene and a minor proportion of styrene relative to the amount intended in the eventual copolymer block. As the copolymerization proceeds, styrene is introduced into the reactor either incrementally or continuously. After the formation of the random copolymer block of styrene and alpha-methyl styrene which block has a lithium ion on the growing end of the polymer chain, a conjugated diene is then introduced to form the elastomeric polymer block B. The polymerization is continued until the desired molecular weight thereof is attained. The intermediate block copolymer then has the general configuration $\text{A}-\text{B}-\text{Li}$, at which point a second block A may be formed by the introduction of styrene and alpha-methyl styrene. The resulting block copolymer will then have the structure $\text{A}-\text{B}-\text{A}$.

The second type of process by which the block copolymers according to the invention may be prepared may be referred to as a coupling process. In this process the intermediate block copolymer $\text{A}-\text{B}-\text{Li}$ is formed as just described and thereafter a coupling agent capable of reacting with the lithium ions is injected into the reaction mixture. The coupling agent may be bifunctional or polyfunctional. The simplest form of coupl-

ing agent is a dihalogen alkane or a divinyl aromatic hydrocarbon such as a divinyl benzene. Typical halogen coupling agents include dibromomethane and dichlorobutane. In such a case the resulting polymer has the configuration $\text{A}-\text{B}-\text{A}$. Multifunctional coupling agents may be used as well. Examples of such coupling agents are epoxides, isocyanates, polyketones, polyaldehydes, triaziridinyl phosphine oxides, or sulphides. A unique type of multifunctional coupling agent is a diester formed between a dicarboxylic acid and a monohydric alcohol, such as diethyl adipate or dimethyl adipate. With the use of multifunctional coupling agents, the resulting block copolymers have a branched configuration which is variously referred to as radical, branched or star-shaped block copolymers.

The third type of process by which the block copolymers according to the invention may be prepared involves the use of a multifunctional initiator. The simplest type of such initiator is one having two metallic ions such as two lithium ions. Examples of such initiators are dilithio-stilbene and dilithium alpha-methyl styrene. A di-initiated polymer is formed with such initiators by first forming a polymer block of elastomeric conjugated diene bearing lithium radicals on both ends of the growing polymer chain. Then a mixture of alpha-methyl styrene and styrene is introduced into the reaction mixture to form two terminal copolymer blocks A. The resulting block copolymer has the structure $\text{A}-\text{B}-\text{A}$.

Subsequent to the preparation of the block copolymers, they may be isolated by coagulation or precipitation or they may be used in the form of their cements. On the other hand, they are in suitable condition for being hydrogenated. For this purpose preferred catalysts are the reduction products formed by reaction of an aluminium alkyl compound e.g., aluminium triethyl with a nickel or cobalt carboxylate, e.g., acetates or octoates or alkoxide, e.g., acetyl acetonates or butoxides. The reduction product of cobalt or nickel carboxylates is especially useful for the complete non-selective hydrogenation of the entire block copolymer. The reduction products of cobalt or nickel alkoxides on the other hand are particularly important for selective hydrogenation of the block copolymers in order to reduce the oxidation sensitivity of the elastomeric diene polymer blocks, in which the unsaturation of the vinyl aromatic hydrocarbon segments is excluded. Thus, conditions and catalysts may be utilized to perform either complete or partial hydrogenation. Hydrogen pressures for this step are of the order of from 7-105 kg/cm², while temperatures are of the order of ambient temperature to 125°C. If the complete polymer is to be hydrogenated, it may be preferred to conduct this in several stages so as to completely hydrogenate the elastomeric blocks at a relatively

lower temperature and then raise the temperature for hydrogenation of the random copolymer blocks of styrene and alpha-methyl styrene.

5 It has been found that the block copolymers according to the invention containing terminal random copolymer blocks of styrene and alpha-methyl styrene have an improved thermal stability in comparison with block copolymers with terminal homopolymer blocks of alpha-methyl styrene. The improvement of the thermal stability is apparently due to the interruption of the alpha-methyl styrene chain. A homopolymer block of alpha-methyl styrene, however, tends to depolymerize on thermal influence. Consequently with copolymerization of styrene with alpha-methyl styrene and with hydrogenation of the blocks B it is possible not only to utilize increased processing temperatures but also to employ the block copolymers so modified at elevated processing temperatures.

The following examples illustrate the present invention.

EXAMPLE I

25 23.6 Grams of alpha-methyl styrene were dissolved in 1,000 ml. of tetrahydrofuran at -20°C . After the careful addition of small traces of sec. butyl lithium, which reacted with impurities present, a light red colour formed immediately. 13.3 ml. of a 0.15 molar solution of sec. butyl lithium in heptane were added and 6.5 grams of styrene monomer were slowly metered into the reaction vessel over a period of 3 hours. After 3 hours 156 grams of gaseous butadiene were introduced into the polymerization mixture followed by polymerization at -10°C for another 3 hours. The resulting living two-block polymer having the structure styrene-alpha methyl styrene block copolymerpolybutadiene-Li was quantitatively coupled by a stoichiometric amount of phenyl benzoate. The isolated dimerized, i.e., coupled block copolymer was found to be highly stable and to possess the properties of a thermoplastic elastomer. The block molecular weights of the styrene-alpha methyl styrene copolymer blocks were about 15,000, while the elastomeric polybutadiene blocks have an average molecular weight of about 78,000.

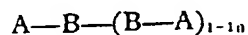
EXAMPLE II

55 To a solution of 65 grams of butadiene in 480 grams of toluene, 13.9 grams of an alpha-methyl styrene-lithium based di-initiator solution (prepared by reacting 2 grams of lithium dispersion with 9.1 grams of alpha-methyl styrene in 326 grams of diethylether at 0°C) corresponding to 2.02 milliequivalents of active lithium were added at 40°C . After 4 hours the polymerization of the butadiene was complete. The polymerization mixture was cooled down to -15°C and 73 grams were removed for analytical samples. After the addition of 300

grams of tetrahydrofuran to the living dilithio-polybutadiene, 22.3 grams of high vacuum line purified alpha-methyl styrene were added. The temperature was lowered immediately to -50°C and 4 grams of pure styrene were introduced slowly into the reaction mixture over a period of 2 hours. The isolated block copolymer was analyzed by nuclear magnetic resonance, infrared and molecular weight determinations. The copolymer blocks had a molecular weight of 65,000 for the elastomeric polybutadiene middle block and 13,000 for each of the end random copolymer blocks of styrene and alpha-methyl styrene. The polybutadiene-middle block showed a 1,2- content of 45%.

WHAT WE CLAIM IS: —

1. A block copolymer having the general configuration



in which each A is a random copolymer block of styrene and alpha-methyl styrene having from 10 to 40 mol. % of styrene units based on the polymerized monomer units of the random copolymer block, and each B is an elastomeric polymer block of a conjugated diene, an elastomeric polymer block of a hydrogenated conjugated diene or a polymer block of an alpha mono-olefin.

2. A block copolymer as claimed in claim 1, in which each A of the block copolymer of the general configuration $\text{A}-\text{B}-(\text{B}-\text{A})_{1-10}$ is a random copolymer block of styrene and alpha-methyl styrene having from 15 to 35 mol. % of styrene units based on the total polymerized monomer units of the random copolymer block, the blocks A having an average molecular weight of between 2,000 and 50,000, and each B is an elastomeric polymer block of a conjugated diene having an average molecular weight of between 15,000 and 100,000.

3. A block copolymer as claimed in claim 1, in which the polymer blocks B are elastomeric polymer blocks of an alpha mono-olefin.

4. A block copolymer as claimed in claim 1, in which the polymer blocks B are elastomeric hydrogenated polymer blocks of a conjugated diene wherein at least 85% of the original unsaturation is reduced by hydrogenation.

5. A block copolymer as claimed in claim 1, in which the polymer blocks B are elastomeric hydrogenated polyisoprene blocks.

6. A block copolymer as claimed in claim 1, in which the polymer blocks B are elastomeric hydrogenated random copolymers of 10—90 mol. % of isoprene with 90—10 mol. % of butadiene.

7. A block copolymer as claimed in claim 1, in which the polymer blocks B are elastomeric

meric hydrogenated polybutadiene blocks with 35—55% 1,2 micro structure.

8. A block copolymer as claimed in claim 1 substantially as hereinbefore described.

5 9. A process for the preparation of a block copolymer having the general configuration A—B—A in which each A is a random copolymer block of styrene and alpha-methyl styrene having from 10 to 40 mol. % of
10 styrene units based on the total polymerized monomer units of the random copolymer block, and B is elastomeric polymer block of a conjugated diene, characterized in that alpha-methyl styrene is polymerized together with
15 styrene using a monofunctional lithium compound as catalyst in a hydrocarbon medium modified with a polar activating compound to form an initial block A, then the polymerization is continued by adding a conjugated
20 diene to the reaction mixture to form the polymer block B which is attached to the initial polymer block A, and finally the polymerization is continued by adding alpha-methyl styrene and styrene to the reaction
25 mixture to form a second polymer block A which is attached to polymer block B.

10. A process for the preparation of a block copolymer having the general configuration A—B—(B—A)₁₋₁₀ in which each A is a
30 random copolymer block of styrene and alpha-methyl styrene having from 10 to 40 mol % of styrene units based on the total polymerized monomer units of the random copolymer units, and each B is an elastomeric
35 polymer block of a conjugated diene, characterized in that alpha-methyl styrene is polymerized together with styrene using a monofunctional lithium compound as catalyst in a hydrocarbon medium modified with a polar
40 activating compound to form an initial polymer block A, then the polymerization is continued by adding a conjugated diene to the reaction mixture to form a polymer block B which is attached to the initial polymer block
45 A to form the intermediate block copolymer A—B—Li and finally a bifunctional or polyfunctional coupling agent is added to the reaction mixture coupling intermediate block copolymers A—B—Li together to form a
50 block copolymer of the general configuration A—B—(B—A)₁₋₁₀.

11. A process for the preparation of a

block copolymer having the general configuration A—B—A— in which each A is a random copolymer block of styrene and alpha-methyl styrene having from 10 to 40 mol. %
55 of styrene units based on the total polymerized monomer units of the random copolymer block, and B is an elastomeric polymer block of conjugated diene, characterized in that a
60 conjugated diene is polymerized in the presence of a dilithio compound as initiator and a hydrocarbon medium modified with a polar activating compound to form a polymer block B bearing lithium atoms on both ends of the
65 growing polymer chain and then the polymerization is continued by adding a mixture of alpha-methyl styrene and styrene to the reaction mixture to form two terminal copolymer blocks A.

12. A process for the preparation of a block copolymer having the general configuration A—B—(B—A)₁₋₁₀ in which each A is a random copolymer block of styrene and alpha-methyl styrene having from 10 to 40% of
75 styrene units based on the total polymerized monomer units of the random copolymer block and each B is an elastomeric polymer block of a hydrogenated conjugated diene or a polymer block of an alpha-mono-olefin
80 characterized in that the block copolymer obtained by a process as claimed in any one of claims 9—11 is hydrogenated by hydrogen under a pressure of from 7 to 105 kg/cm² at
85 a temperature of between ambient temperature and 125°C, and the presence of a hydrogenation catalyst.

13. A process as claimed in any one of claims 9 to 12 substantially as hereinbefore described.

14. Block copolymer whenever obtained by a process as claimed in any one of claims 9—13.

15. A formed article prepared from a block copolymer as claimed in any one of claims 1—8.

16. A formed article prepared from a block copolymer as claimed in claim 14.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.